Development of a molten salt system for thermal energy storage at elevated temperatures

Nicole Pfleger, Thomas Bauer, Markus Braun, Markus Eck, Doerte Laing

Overview

- Characterization of salt systems:
  - thermal stability
  - thermodynamical properties (Cp ~ costs)
  - availibility
  - handling

- Optimization of salt system:
  reducing the melting temperature for increased storage capacity:
  - traditional approach
  - new method

Definition of salt system

cations:

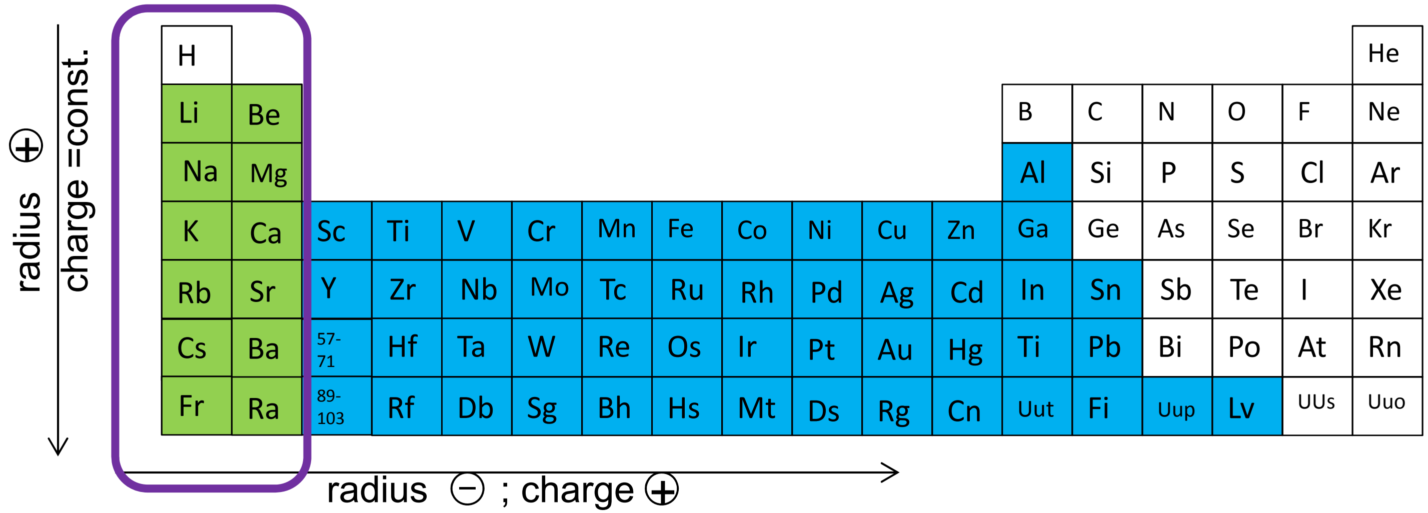
single element cations:

-> no decomposition for cations takes place

anions:

- sulfate
- carbonate
- fluoride/ chloride/ bromide/ iodide

Suitable cations



stability of polyatomic anion $\overset{\ominus}{\longleftrightarrow}$ polarization power of associated cation $\overset{\ominus}{\longleftrightarrow}$ $\frac{r^{1/2}}{Z}$ r = radius, Z= charge

=> Cations : alkali metals / alkaline earth metals

Extent of theoretical research:

anion groups	: 6
single salts	: 50
salt mixtures	: 180

Result of anion groups:

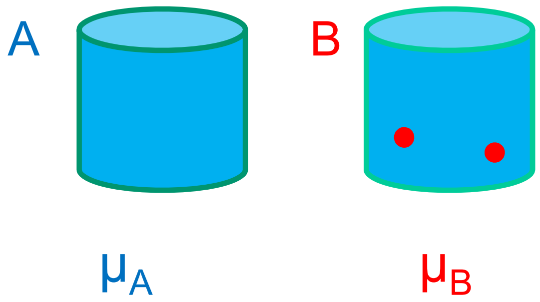
Fluoride F^- → toxic/ corrosive

Bromide Br^-
Iodide I^- → expensive

Carbonate CO_3^{2-}
Chloride Cl^-
Sulfate SO_4^{2-} → suitable

	Carbonate	Chloride	Sulfates
	▪ High thermal stability >1200 °C ▪ High heat capacity >1.5 J/gK ▪ Not corrosive	▪ High thermal stability > > 1200 °C ▪ Cheap	▪ High thermal stability >1000 °C ▪ High heat capacity >1.2 J/gK
	▪ High melting point >800 °C	▪ Low heat capacity (~1 J/ gK) ▪ Quite corrosive ▪ High melting point	▪ High melting point >880 °C

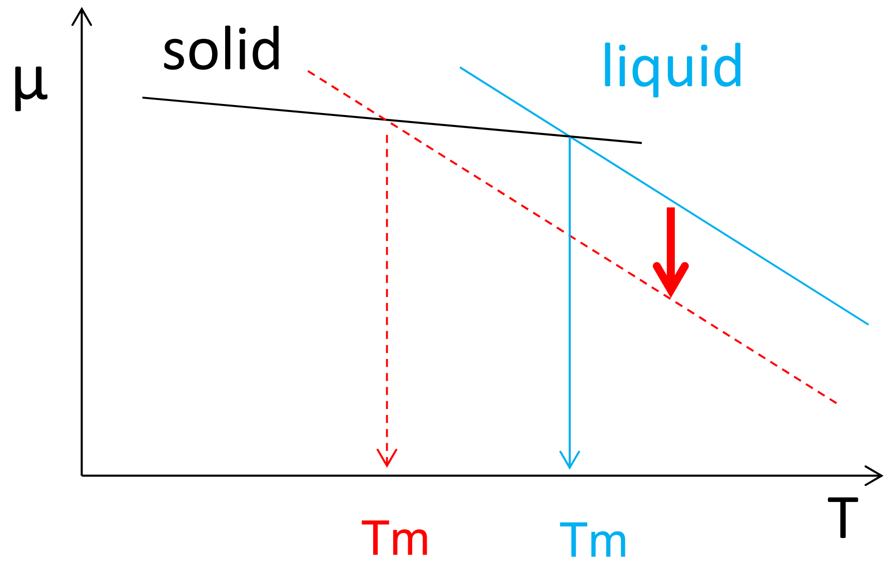
Reduction of melting point



x := ratio of second component

$(d\mu/dT)_p = -S$

$\mu_B - \mu_A = RT \ln(1-x);$



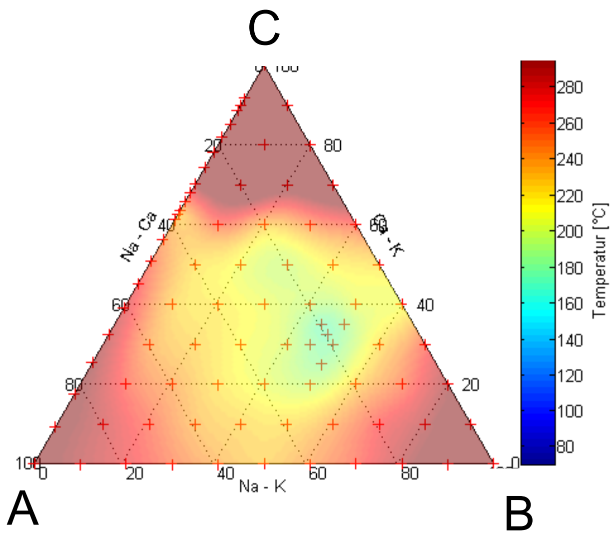
➔ Mixing reduces Tm (if component is insoluble in the solid)

DLR

Reduction of melting temperature by high troughput screening

Determination of melting temperatures of samples by DSC (differential scanning calorimetry)

- Advantage:
  - Applicable to all conceivable salt mixtures
- Disadvantage:
  - For every system numerous salt compositions have to be analyzed

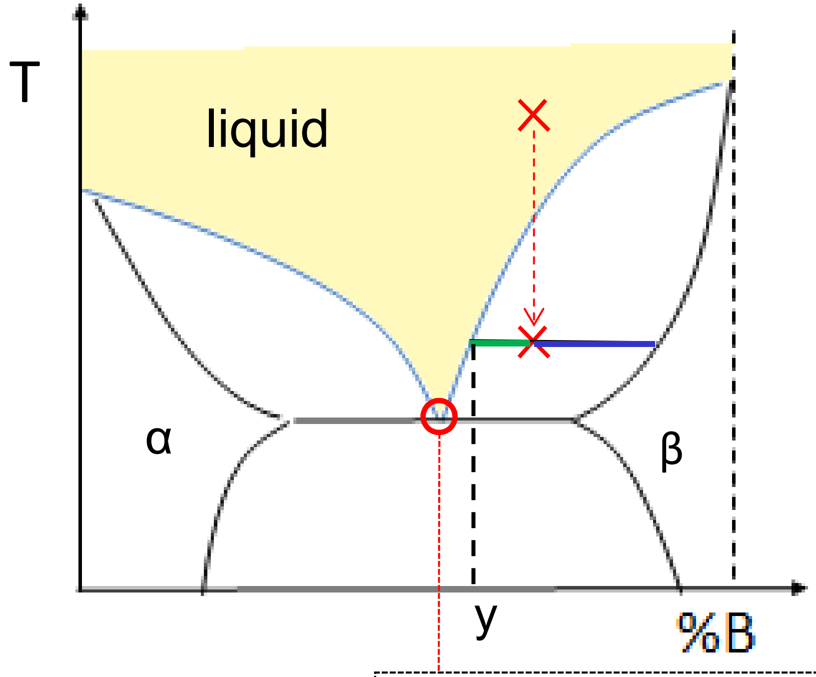


DLR

Binary systems

Temperature dependancy and composition depenency:

- number and type of phases
- ratio $^{liquid}/_{solid}$
- ratio $^{[A]}/_{[B]}$



→ Reduction of the temperature

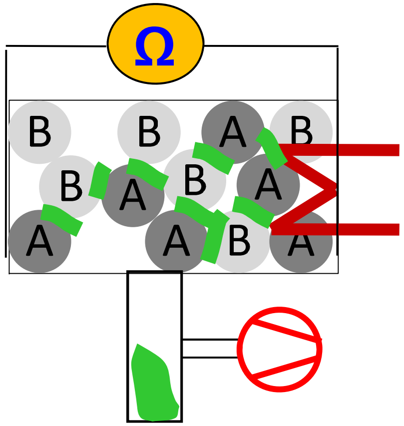
changed composition of liquid phase

composition with lowest melting temperature

Innovative synthesis

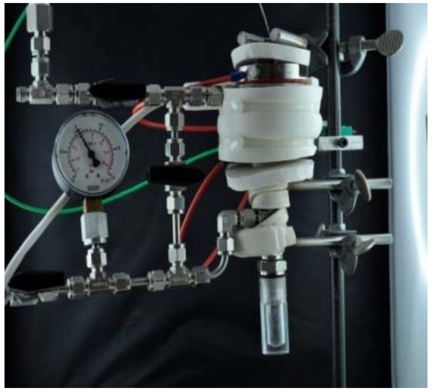
•Preparation of pellet

with A and B



•Slow heating

$T \approx T_{melt}$



container 1

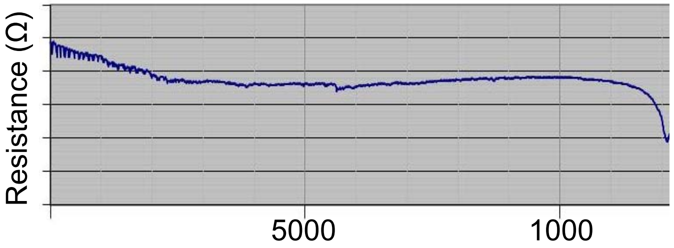
container 2

evacuation system

•Liquid phase formation

+ detection

(by electric resistance)

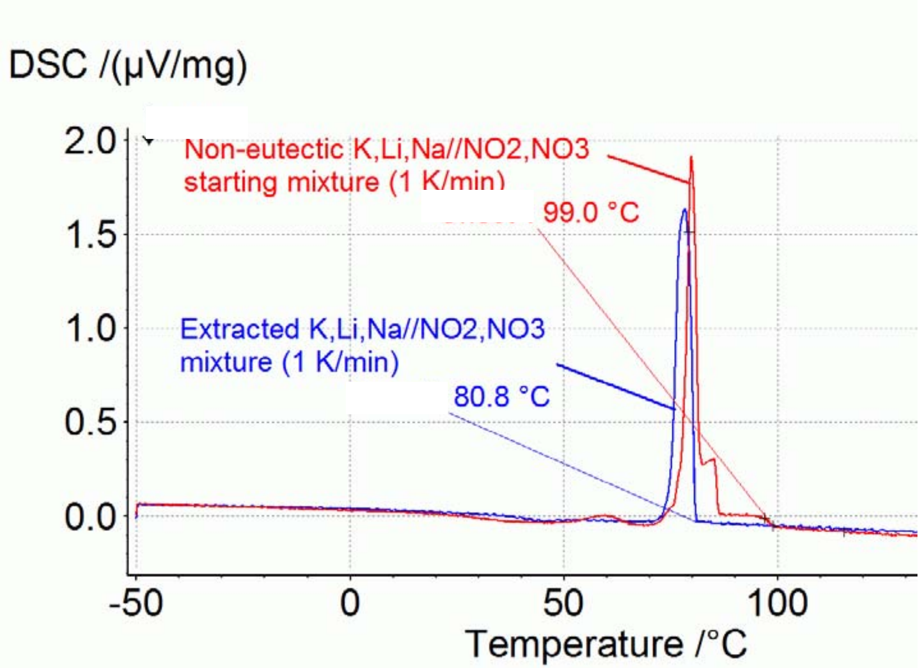


•extraction

(by applying vacuum)

Validation for low temperature system

- Known System[1] of K,Li,Na//NO_2,NO_3
- Starting with non-eutectic mixture (red DSC line)
- Heating to "start of melting temperature" (solidus)
- Extraction of liquid phase
- Composition of extracted mixture is eutectic (blue DSC line)



-[1]J.G. Cordaro, N.C. Rubin, M.D. Sampson, R.W. Bradshaw (2010) *Multi-Component Molten Salt Mixtures based on*

-*Nitrate/Nitrite Anions*, Paper presented at the Solar Paces, 21.-24. Sep., Perpignan, France

Results for high temperature systems:

- Chloride :NaCl-KCl-$MgCl_2$ (24-21-55) [(1),(2)]

Melting temperature	Heat capacity	Thermal conductivity	density
393°C	1 J/gK	0.95 W/ mK	1 800 kg/m^3

- Carbonate: Li_2CO_3-Na_2CO_3-K_2CO_3 (43.5-31.5-25) [(3)]

Melting temperature	Heat capacity	Thermal conductivity	density
397°C	1.63 J/gK	2.02 W/ mK	2140 kg/m^3

(1) Murat M. Kenisarin (2010) High-temperature phase change materials for thermal energy storage

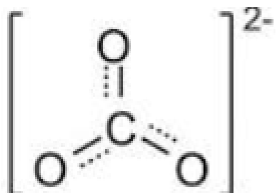
(2) G.J. Janz, R.P.T. Tomkins: Physical Properties Data Compilations Relevant to Energy Storage. IV. Molten Salts: Data on Additional Single and Multi-Component Salt System

(3) M.Geyer (1990) A feasibility study on thermal energy storage for commercial applications

DLR

Conclusions

Cl^-



Storage media for high temperature applications:
- Chloride systems/ Carbonate systems (400 °C - 800 °C)
- Further investigations required for lower T_{melt}

Methods for reducing melting temperature:
- High throughput method
- Extraction-by-vakuum method (to be extended for high T)